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(71) Applicant: SRI INTERNATIONAL [US/US]; 333 Ravenswood Avenue, Menlo Park, CA 94025 (US).

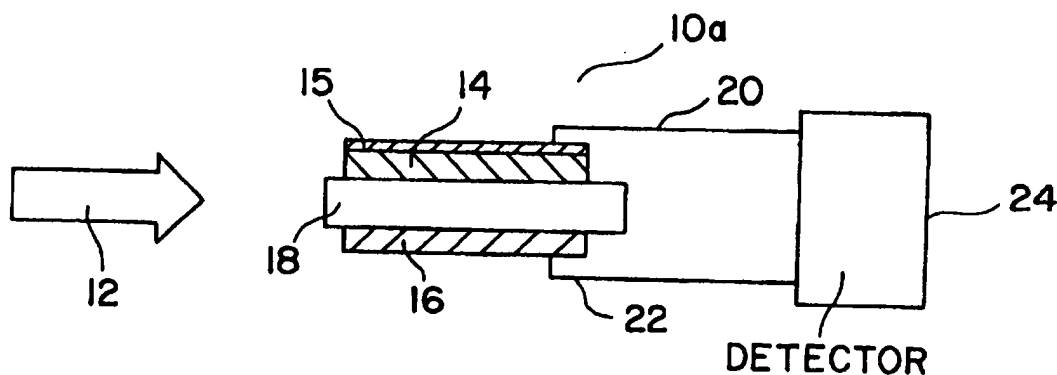
(72) Inventors: WACHSMAN, Eric, D.; 5400 N.W. 39th Street #T-171, Gainesville, FL 32606 (US). JAYAWEERA, Palitha; 34272 Lennox Court, Fremont, CA 94555 (US).

(74) Agents: BAROVSKY, Kenneth; Reed & Associates, Suite 200, 285 Hamilton Avenue, Palo Alto, CA 94301 (US) et al.

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(54) Title: SOLID STATE ELECTROCHEMICAL CELL FOR MEASURING COMPONENTS OF A GAS MIXTURE, AND RELATED MEASUREMENT METHOD



(57) Abstract

A solid state electrochemical cell is provided for measuring components of a gas mixture. The sensor comprises at least one semiconductor electrode comprising a semiconducting material, a metal electrode and an electrolyte in contact with the semiconductor electrode and the metal electrode. The sensor optionally includes a reference electrode encased in a chamber to isolate the reference electrode from the gas mixture. In addition, methods are provided for measuring the concentrations of components of a gas mixture.

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SOLID STATE ELECTROCHEMICAL CELL
FOR MEASURING COMPONENTS OF A GAS MIXTURE,
AND RELATED MEASUREMENT METHOD

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TECHNICAL FIELD

The present invention relates generally to measurement of components in a gas stream, and more particularly relates to a novel
10 electrochemical cell and method for measuring the concentration of oxides in a gas mixture.

BACKGROUND

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Various devices and methods have been described for determining the concentration of oxides of nitrogen (NO_x , for example, N_2O , NO and NO_2), oxides of carbon (CO_x , for example, CO and CO_2), oxides of sulfur (SO_x , for example, SO_2 and SO_3), other oxide compounds in a gas mixture,
20 which may include gaseous oxygen (O_2), nitrogen (N_2), other inert gases, as well as combustible gases such as H_2 and hydrocarbons.

The presence and concentration of gaseous oxide compounds have been measured using electrochemical sensing devices and methods. Typically, such devices and methods have been based on the "oxygen pumping principle," that has been described in, for example, U.S. Patent No. 4,005,001 to
25 Pebler, U.S. Patent No. 4,770,760 to Noda et al., U.S. Patent No. 4,927,517 to Mizutani et al., U.S. Patent No. 4,950,380 to Kurosawa et al., U.S. Patent No. 5,034,107 to Wang et al., and U.S. Patent No. 5,034,112 to Murase et al.

Generally, a solid electrolyte conductive to oxygen ions is used
30 in a device based on the oxygen pumping principle. The electrolyte is commonly zirconia (ZrO_2), bismuth oxide (Bi_2O_3), ceria (CeO_2), ZrO_2 , Bi_2O_3 and/or CeO_2 containing alkaline earth dopants such as calcia (CaO), or containing rare

earth dopants, such as yttria (Y_2O_3), as a stabilizer, or some other suitable electrolyte having high permeability (conductance) to oxygen when biased at a constant voltage and when maintained above a certain temperature, for instance, greater than $200^\circ C$ in many applications. These electrolytes can selectively permit
5 oxygen to pass therethrough if certain biasing and temperature conditions are met. In other words, these electrolytes exhibit high conductivity at elevated temperatures and application of a voltage creates an O^{2-} current or flux.

In sensors using these oxygen ion-permeable electrolytes, electrodes are generally disposed on opposing surfaces of the electrolyte and a
10 voltage is applied across the electrolyte via the electrodes. The electrodes typically comprise platinum (Pt), rhodium (Rh) and/or other noble metals. In this configuration, the combination of the electrodes and the electrolyte forms an electrochemical cell referred to as a "pumping cell" because it pumps oxygen from the gas mixture exposed to the pumping cell. The pumping cell causes oxygen in
15 the gas mixture to be reduced to oxygen ions at the negative electrode, and then the oxygen ions move through the electrolyte to the positive electrode where they are oxidized to oxygen and discharged.

Numerous techniques have been proposed for determining the amount of oxygen and/or oxide compounds in the environment using
20 electrochemical cells, particularly pumping cells, by monitoring the voltage and/or current generated across and/or through the electrolyte. One type of sensor is described in U.S. Patent No. 5,217,588 to Wang. This sensor uses two electrochemical cells on a zirconia electrolyte. One cell senses only oxygen gas and the other cell senses all the gases which contain oxygen, including the oxygen
25 gas. Both electrochemical cells are exposed to the same gas mixture, and the differences between the sensed signals is a measure of the concentration of NO_x in the gas mixture.

U.S. Patent No. 5,034,112 to Murase et al. describes a sensor in which a catalyst for reducing NO_x is placed on an electrolyte adjacent to a
30 pumping cell. A current is induced in the pumping cell to control the oxygen concentration in the environment around the pumping cell. When the oxygen concentration is depleted to a predetermined level, the catalyst supposedly begins

to deplete NO_x , and the oxygen concentration of NO_x is determined by measuring the current supplied to the pumping cell.

Unlike the electrochemical cell of the invention, these sensors do not provide for highly accurate measurement of NO_x or other oxide compounds in gas mixtures, because the electrodes used for the electrochemical cells are not sufficiently selective with respect to oxygen and oxide compounds, particularly NO_x . Moreover, if the gas mixture contains a relatively low oxide concentration compared with that of oxygen, an accurate determination of the oxide concentration is difficult. In exhaust gases or emissions produced by internal combustion engines or furnaces, the concentration of oxygen is typically several thousand fold higher than the NO_x concentration. Thus, it is difficult to accurately measure NO_x concentration in these gas mixtures using the typical pumping cell.

Another type of sensor described in U.S. Patent No. 5,397,442 to Wachsmann seeks to obviate this problem by providing a sensor including a chamber designed to receive a gas mixture in which two electrochemical cells are situated. Each cell is comprised of an electrode housed inside the chamber and an electrode outside the chamber, in which the internal and external electrodes are separated by an oxygen ion-conducting electrolyte. The first electrochemical cell is designed to consume oxygen by electrochemical reduction without appreciably consuming NO_x , while the second electrochemical cell is relatively selective for the electrochemical reduction of NO_x . A potential difference is applied across the first cell so that oxygen is removed from the chamber and then an electrical characteristic (voltage, current, power, etc.) of the second cell is measured that corresponds to the concentration of the oxide in the gas mixture. However, this system is somewhat complex and, because entry of gas into the chamber is diffusion limited, the response time of the sensor can be relatively slow.

The present invention is based on the discovery that, even in the absence of a diffusion chamber, a sensor that includes an electrochemical cell composed of an electrode made of a semiconducting material, a metal electrode, and an electrolyte in contact with the electrodes displays electrical characteristics that correspond to the presence and concentration of one or more components of

the gas mixture. The present electrochemical cell provides a number of advantages over systems of the prior art. First, the invention allows the accurate and selective detection of NO_x , CO_x , SO_x , other oxides and/or other components in a gas mixture using only one electrochemical cell, i.e., only two electrodes one of which is selective for a chosen component. Second, both electrodes are in the same gas mixture, rather than in separate sample and reference chambers, thereby simplifying manufacture. The present sensors can be produced with small geometries and materials requirements using standard microlithography-semiconductor manufacturing techniques. Third, the invention operates by simply measuring an electrical characteristic of the electrochemical cell without the need to apply a voltage or current across a first set of electrodes and measuring a response of a second set of electrodes. The sensor thus produces a continuous signal that requires little or no amplification. Fourth, the invention can be configured for the accurate and simultaneous detection of two or more components of the gas mixture. Fifth, the response time of the sensor is sufficiently rapid to permit active feedback control of engine function.

RELATED ART

In addition to that summarized above, the following references relate to devices and/or methods for detecting components in a gas mixture:

U.S. Patent No. 4,055,011 to Pebler describes a combustible gas sensor. The reference describes a device that includes first and second electrodes disposed on either surface of an oxygen ion-conducting solid electrolyte; both electrodes are exposed to the gaseous mixture of oxygen and combustible gases such as CH_4 , H_2 , CO , and the like. The electrodes are composed of different materials that exhibit different catalytic combustion activity. The resultant difference in oxygen potential at the electrodes produces an electrical signal that is proportion to the amount of combustible material in the gas mixture. Suitable electrodes include either gold or silver as one electrode and a group VIII metal, such as platinum, palladium and rhodium, as the second electrode. The

operational characteristics of the sensor depend on the different activities by which the electrodes catalyze the combustion of fuels, and hence the demand for oxygen at the respective electrodes, within the gas mixture.

U.S. Patent No. 5,304,294 to Wang et al. relates to a NO_x sensor that employs an electrolyte material sandwiched between two electrodes having different NO_x decomposition characteristics. The sensing principle that forms the basis of this sensor is the decomposition of NO_x to O_2 and N_2 . The different decomposition characteristics result in different decomposition rates at the electrodes and the resultant electromotive force that develops. The decomposition difference may be imparted by a difference in the size of the electrodes (in which case the electrodes may be exposed to the same gas stream), a difference in the composition of the electrodes (e.g., platinum and rhodium), the gas environment to which the electrodes are exposed due to placement of one in a chamber, and the like.

U.S. Patent No. 5,401,372 to Liu et al. relates to an apparatus for removing NO_x from an O_2 -containing exhaust emission by an electrochemical catalytic reduction process. The apparatus is composed of a solid oxide electrolyte with a porous anode (e.g., silver or another electrically conductive metal) and a porous, catalytic cathode such as transition metal oxides to which is abutted an electron-collecting layer such as a conductive perovskite-type oxide.

U.S. Patent No. 5,409,591 to Baker et al. describes a NO_x sensor that uses a mobile cation electrolyte that selectively transmits nitrosonium cations (NO^+) such as nitrosonium β -alumina electrolyte.

Morita et al. (1993) *Chemical Sensors II*, Butler et al., eds., 93-7:450-455 (Electrochem. Soc., Pennington, NJ), describes the semiconducting properties (e.g., resistivity) of La_2CuO_4 upon adsorption of positively charged NO and negatively charged NO_2 ions. The changes in resistivity (increase by NO and decrease by NO_2) are proposed to be due to surface adsorption of these gases, and the respective injection and withdrawal of electronic charge into the material. However, Morita et al. does not discuss the use of an electrolyte in contact with such a semiconducting material and a second electrode not displaying semiconducting properties.

Tamaki et al. (1993) *Chemical Sensors II*, Butler et al., eds., 93-7:456-463 (Electrochem. Soc., Pennington, NJ), describes a tungsten oxide (WO_3)-based NO_x sensor. Changes in the resistance of a sintered WO_3 powder sensor is due to the adsorption of NO_x on WO_3 particles which thereby create an electron-depleted space charge layer in the surface region of the WO_3 particle. Like Morita et al., *supra*, Tamaki et al. does not discuss the use of an electrolyte in contact with a semiconducting material and a second nonsemiconducting electrode.

10

DISCLOSURE OF THE INVENTION

Accordingly, it is a primary aim of the invention to address the above-mentioned needs in the art by providing a solid state electrochemical cell for measuring the concentration of a component of a gas mixture.

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It is another aim of the invention to provide an electrochemical cell for measuring the concentration of a component of a gas mixture that includes a semiconductor electrode that comprises semiconducting material, a metal electrode and an electrolyte in contact with both the semiconductor and metal electrodes.

20

It is still another aim of the invention to provide an electrochemical cell for measuring two or more component in a gas mixture that includes a set of semiconductor electrodes, a metal electrode and an electrolyte in contact therewith.

25

It is yet another aim of the invention to provide a method for measuring the concentration of components of a gas mixture.

30

Additional aims, advantages and novel features of the invention will be set forth in part in the description which follows, and in part will become apparent to those skilled in the art upon examination of the following, or may be learned by practice of the invention.

In one aspect, then, an electrochemical cell for measuring the concentration of a component of a gas mixture is provided. The electrochemical

cell comprises a semiconductor electrode, a metal electrode, each of which have first and second opposing surfaces, and an electrolyte in contact with the second surface of each of the semiconductor and metal electrodes. The semiconductor electrode comprises a semiconducting material selected so as to undergo a change
5 in resistivity upon contacting the component of the gas mixture. The electrochemical cell is structured such that when the first surface of the semiconductor or metal electrode contacts the gas mixture, the first surface of the other of electrode necessarily contacts the gas mixture as well.

In another aspect of the invention, an electrochemical cell for
10 measuring the concentration of two or more components of a gas mixture is provided. The electrochemical cell comprises a set of semiconductor electrodes, each of which comprises a semiconducting material selected so as to undergo a change in resistivity upon contacting a particular component in the mixture, a metal electrode, and an electrolyte in contact with the set of semiconducting
15 electrodes and the metal electrode.

In still another aspect of the invention, a method for measuring the concentration of a component of a gas mixture is provided. The method comprises exposing the gas mixture to an electrochemical cell including a semiconductor electrode, a metal electrode and an electrolyte in contact with the
20 semiconductor and metal electrodes, and measuring an electrical characteristic associated with the semiconductor and metal electrodes to determine the concentration of the component of the gas mixture.

In yet another aspect of the invention, a method for measuring the concentration of two or more components of a gas mixture is provided. The
25 method comprises exposing the gas mixture to an electrochemical cell that includes a set of semiconductor electrodes that are semiconducting materials, a metal electrode and an electrolyte in contact therewith, and measuring an electrical characteristic associated with one of the set of semiconductor electrodes and the metal electrode to determine the concentration of the component of the gas
30 mixture.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1A, 1B, and 1C schematically illustrate first, second, and third embodiments of a solid state electrochemical cell as disclosed herein.

5 FIG. 2 depicts the response in millivolts of a sensor configured as shown in FIG. 1A in which the semiconducting material was La_2CuO_4 as a function of NO concentration in 25% O_2 .

10 FIG. 3 depicts the response in millivolts of a sensor configured as shown in FIG. 1A in which the semiconducting material was La_2CuO_4 as a function of: (a) NO concentration in 25% O_2 ; and (b) O_2 concentration with 500 ppm NO.

15 FIG. 4 depicts the response in millivolts of a sensor configured as shown in FIG. 1A in which the semiconducting material was La_2CuO_4 as a function of NO concentration with 13% O_2 (•), 15% O_2 (■) or 17% O_2 (▲) in a simulated exhaust gas.

20 FIG. 5 depicts the response in millivolts of a sensor configured as shown in FIG. 1A in which the semiconducting material was La_2CuO_4 as a function of NO concentration with 1000 ppm CO (•) or 2000 ppm CO (◻) in a simulated exhaust gas.

25 FIG. 6 depicts the response in arbitrary units (a.u.) of a sensor configured as shown in FIG. 1A in which the semiconducting material was La_2CuO_4 to a 50 ppm pulse of NO in a simulated exhaust gas.

 FIG. 7 depicts the response in millivolts of a sensor configured as shown in FIG. 1A in which the semiconducting material was $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Co}_{0.9}\text{Ru}_{0.1})\text{O}_3$ as a function of NO concentration in a simulated exhaust gas.

 FIG. 8 depicts the response in arbitrary units (a.u.) of a sensor configured as shown in FIG. 1A in which the semiconducting material was $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Co}_{0.9}\text{Ru}_{0.1})\text{O}_3$ to a 50 ppm pulse of NO in a simulated exhaust gas.

MODES FOR CARRYING OUT THE INVENTION

It is to be understood that this invention is not limited to specific semiconducting materials, specific electrolytes, specific metals, or to particular apparatus configurations as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only and is not intended to be limiting.

It must be noted that, as used in the specification and the appended claims, the singular forms "a", "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a semiconducting material" includes mixtures of semiconducting materials, reference to "an electrolyte material" includes mixtures of two or more electrolyte materials, reference to "an electrode" includes two or more such electrodes, and the like.

In this specification and in the claims which follow, reference will be made to a number of terms which shall be defined to have the following meanings:

The term "NO_x" is intended to refer to any molecular species consisting of nitrogen and oxygen, e.g., NO, NO₂, N₂O, N₂O₄, or combinations thereof.

The term "gas mixture" is used to refer to a gas containing one or more components to which the sensor is exposed during operation. A gas mixture may be, for example, the exhaust gas from an internal combustion engine, furnace or other source.

The term "electrolyte" is used in its conventional sense to indicate a nonmetallic conductor in which current is carried by the movement of ions. For example, an "oxygen ion-conducting electrolyte" is one in which the current is carried by oxygen ions.

The term "semiconductor" or "semiconducting material" is used herein in its usual sense to indicate a crystalline solid material with an electrical conductivity intermediate between that of a conductor and an insulator. A summary of the physics and properties of semiconductors can be found in, for

example, Sze (1981) *Physics of Semiconductor Devices*, 2nd edn., John Wiley & Sons (New York), the disclosure of which is incorporated herein by reference.

By a "set of electrodes" is intended two or more discrete electrodes that are individually responsive to different components of a gas mixture. Thus, for example, one electrode of the set may be responsive to NO,
5 another of the set of electrodes may be responsive to CO, and still another of the set may be responsive to SO₂.

The phrase "electrochemical cell" and the term "sensor" are used interchangeably herein to mean a device for measuring the concentration of one or more gaseous compounds. An electrochemical cell containing a set of
10 electrodes is capable of simultaneously measuring the concentration of more than one component of a gas mixture.

"Optional" or "optionally" means that the subsequently circumstance may or may not occur, and that the description includes instances in which said circumstance occurs and instances in which it does not. For example,
15 the phrase "optional metal layer" means that a metal layer may or may not be present and that the description includes both the instance when the metal layer is present and the instance when the metal layer is not present.

Referring now to the drawings, wherein like reference numbers designate corresponding parts throughout the several embodiments, a sensor 10a,
20 10b, 10c of FIG. 1 is disposed in a stream of a gas mixture 12, such as exhaust or emission for an engine or furnace, for measuring the concentration of a component in the gas mixture, including but not limited to NO_x, CO_x, SO_x, or the like.

In one embodiment, shown in FIG. 1A, sensor 10a includes an electrochemical cell defined by semiconductor electrode 14 and metal electrode 16
25 and an electrolyte 18 in contact with the semiconductor and metal electrodes. As shown in FIG. 1A, as well in FIG. 1B and FIG. 1C, *infra*, the electrolyte is disposed between the electrodes. However, both semiconductor electrode 14 and metal electrode 16 may be situated on the same surface of the electrolyte. Sensor
30 10a is configured so that when semiconductor electrode 14 is exposed to the gas stream metal electrode 16 is necessarily exposed to the gas stream as well.

Semiconductor electrode 14 is a semiconducting material. The semiconducting material may be an *n*-type or a *p*-type semiconducting material. The semiconducting material is selected to undergo a change in conductivity or resistivity upon contacting the component of interest in the gas mixture. The semiconductor may be a metal oxide or a metal oxide compound. The terms "metal oxide" and "metal oxide compound" are used interchangeably herein to mean a compound having an elemental metal combined with O₂. Examples of metal oxides that are useful in the invention include tin oxide (SnO₂), zinc oxide (ZnO), mixtures thereof, and the like. In one embodiment the metal oxide compound has a perovskite lattice structure. By "perovskite lattice structure" is intended a mixed metal oxide lattice structure having at least two different metals combined with oxygen to form a cubic structure (point symmetry *m3m*) made up of a regular array of corner-sharing oxygen octahedra with smaller highly charged cations like Cu, Co, Mn, Ru, Ti, Sn, Zr, Nb, Ta, W, etc., occupying the central octahedral B site, and lower-charged larger cations such as Bi, La, Na, K, Rb, Ca, Sr, Ba, Pb, etc., filling the interstices between octahedra in the larger 12-coordinated A sites. The structure for many mixed metal oxides that form a perovskite lattice structure is ABO_x, in which A and B are different metals and x is any number, but preferably approximately 3. However the perovskite structure is tolerant of a wide variety of multiple cation substitutions in both A and B sites such that perovskites can be formed having the formula A_{n-x}A'_xB_{m-y}B'_yO_z, in which A and A' are the same or different metals, B and B' are the same or different metals, and wherein at least one of A and A' is a different metal from B and B', n and m are integers typically less than 100, preferably in the range of 1 to 10, most preferably 1 to 4, and x, y and z are stoichiometric compositional fractions such that valence requirements are satisfied for maintaining the lattice structure. Further, a "perovskite" means any compound having, at least, a perovskite lattice structure. Examples of perovskites include La₂CuO₄, LaNiO₃, LaFeO₃, LaCoO₃, LaMnO₃, (La_{0.75}Sr_{0.25})CoO₃, (La_{0.8}Sr_{0.2})(Co_{0.9}Ru_{0.1})O₃, (K_{0.5}Bi_{0.5})TiO₃, Pb(Fe_{0.5}Ta_{0.5})O₃, Pb(Co_{0.25}Mn_{0.25}W_{0.5})O₃, and the like. One of ordinary skill in the art will recognize that the actual oxygen stoichiometry will vary depending on the metals that occupy the A and B sites of the lattice

structure as well the different valences of the metals at a given site. Accordingly, the numbers of oxygen atoms indicated herein approximate the actual stoichiometric amount of oxygen that will be found in a given composition.

The choice of material for semiconductor electrode 14 is determined by the component of the gas mixture to be measured. Materials that are selectively responsive, i.e., that undergo a change in resistance, to particular gases are well known in the art. For example, to measure the concentration of NO in a gas mixture, semiconductor electrode 14 may be La_2CuO_4 . As shown in Example II, $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Co}_{0.9}\text{Ru}_{0.1})\text{O}_3$ may also be used as a material for semiconductor electrode 14 to measure NO in a gas mixture. In addition, mixtures of La_2CuO_4 and $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Co}_{0.9}\text{Ru}_{0.1})\text{O}_3$ may be used for electrode 14 as well. The concentration of NO_2 or NH_3 in a gas mixture may be measured using an electrochemical cell in which semiconductor electrode 14 is respectively a rare earth cuprate (e.g., $\text{Tm}_2\text{Cu}_2\text{O}_5$ and $\text{Yb}_2\text{Cu}_2\text{O}_5$; see Imanaka et al. (1995) *J. Electrochem. Soc.* 142:1950) or In_2O_3 doped with MgO (see Takao et al. (1994) *J. Electrochem. Soc.* 141:1028). To measure the concentration of CO, semiconductor electrode 14 may comprise SnO_2 , ZnO, In_2O_3 , and mixtures thereof, optionally containing other metals or metal oxides added to enhance CO selectivity (see Yamaura et al. (1996) *J. Electrochem. Soc.* 143:L36 (In_2O_3 with Rb_2O), Fukui et al. (1995) *Sensors and Actuators B* 24-25:486 (SnO_2 with $\text{Au-La}_2\text{O}_3$), and Nitta et al. (1979) *J. Electronic Materials* 8:571 (SnO_2 with ThO_2)). SO_2 may be measured using a metal sulfate such as Li_2SO_4 , $\text{Li}_2\text{SO}_4\text{-CaSO}_4\text{-SiO}_2$ (4:4:2 in molar ratio) or $\text{Li}_2\text{SO}_4\text{-MgO}$ (8:2) for semiconductor electrode 14 (see Yan et al. (1966) *J. Electrochem. Soc.* 143:609). Other components of a gas mixture may be measured using an electrochemical cell in which semiconductor electrode 14 is made of other materials, for example: an SnO_2/CuO heterocontact (H_2S ; see Devi et al. (1995) *J. Electrochem. Soc.* 142:2754 and Maekawa et al. (1993) *Proc. Symp. Chem. Sensors II* 93-7:287); a pure CuO/ZnO heterocontact (H_2 ; see Jung et al. (1994) *J. Electrochem. Soc.* 141:L53); an SnO_2 film in a $\text{SiO}_2/\text{SnO}_2$ layered structure (H_2 and CH_4 ; see Feng et al. (1993) *Proc. Symp. Chem. Sensors II* 93-7:538); ZnO (trimethylamine, dimethylamine; Nanto et al. (1993) *Proc. Symp. Chem. Sensors II* 93-7:522).

Metal electrode 16 is, for example, silver, gold, rhodium, or a noble metal such as platinum, and does not display a change in resistance upon exposure to the gas mixture. The metal electrode provides an equilibrium reference between the conductive ions and the corresponding gas, e.g., oxygen ions and O_2 . In addition, the metal electrode serves as an electronic conductor to complete the circuit necessary to measure the electrical characteristic of the sensor.

The choice of material for electrolyte 18 depends on the component in the gas mixture to be measured. Thus, to measure the concentration of an oxide component, for example, NO_x , CO_x or SO_x , the electrolyte is preferably an oxygen-ion conducting electrolyte. Preferred oxygen ion-conducting electrolytes are zirconia (ZrO_2), bismuth oxide (Bi_2O_3), ceria (CeO_2), mixtures of the foregoing compounds optionally with one or more dopants, such as calcia (CaO) or yttria (Y_2O_3) as a stabilizer, or some other suitable oxygen ion-permeable material. Electrolytes that conduct ionic species other than oxygen ions, e.g., halides, are well known in the art and also find utility in the invention for measuring halogen-containing gas species.

Electrodes 14 and 16 are respectively connected by leads 20 and 22 to a suitable detector 24 that measures an electrical characteristic, e.g., the voltage or current, of the electrochemical cell. The measured electrical characteristic is proportional to the concentration of the component in the gas mixture. A sensor configured as illustrated in FIG. 1A, and data generated therewith as shown in FIGS. 2 through 8, are described in Examples I and II.

Semiconductor electrode 14 is optionally coated with metal layer 15. The presence of metal layer 15 on the electrode increases the signal-to-noise ratio and results in enhanced selectivity with respect to the component of the gas mixture being measured. Metal layer 15 is, for example, silver, gold, rhodium, or a noble metal such as platinum, as described above with respect to metal electrode 16. Metal layer 15 may be coterminous with semiconductor electrode 14 or may be applied to semiconductor electrode 14 at the point of attachment of lead 20. Metal layer 15 need not cover the entire exposed surface of semiconductor electrode 14 and may cover as little as about 2 percent to about

50 percent of the exposed surface, and may cover more than 50 percent, preferably 90 percent and more preferably 100 percent of the exposed surface of semiconductor electrode 14. Furthermore, metal layer 15 need not be a continuous layer of metal on the exposed surface of semiconductor electrode 14, but may be formed in any pattern desired, e.g., a cross-hatch pattern, a serpentine pattern, a dotted pattern, or the like, or even a random pattern. Metal layer 15 may be applied to semiconductor electrode 14 using any method well known in the art to achieve a layer thickness of about 1 μm to about 1000 μm , preferably about 50 μm to about 500 μm , and more preferably about 100 μm to about 250 μm .

10 In a second configuration, illustrated in FIG. 1B, a multifunctional sensor 10b is shown including reference electrode 30. Reference electrode 30 is encased in chamber 32 so as not to contact the gas mixture to which electrodes 14 and 16 are exposed. An electrical characteristic of reference electrode 30 relative to metal electrode 16 is measured by connecting the electrodes to a appropriate detecting device, which may or may not be the same device to which electrodes 14 and 16 are connected. The composition of reference electrode 30 is selected to allow measurement of a selected gas component of the gas mixture. For example, to measure the concentration of oxygen in the gas mixture using the reference electrode, i.e., the partial pressure of oxygen (" pO_2 "), reference electrode 30 is composed of a mixture of a metal and the corresponding metal oxide, for example, Ni/NiO, Cu/CuO, or the like.

An additional embodiment of the invention is illustrated in FIG. 1C. Multifunctional sensor shown generally at 10c includes a set of semiconductor electrodes 34 each of which is a semiconducting material that undergoes a change in conductivity or resistivity upon contacting the components of the mixture. Each of the set of semiconductor electrodes 34 is chosen to be selectively responsive to a particular component of the gas mixture, thereby allowing the simultaneous measurement of the concentration of more than one component of the gas mixture. Thus, semiconductor electrodes 34a, 34b, and 34c may be La_2CuO_4 , In_2O_3 doped with Rb_2O , and $\text{Li}_2\text{SO}_4\text{-MgO}$ (8:2), respectively, and allow the simultaneous measurement of NO, CO and SO_2 . Optionally,

semiconductor electrodes 34a, 34b, and/or 34c are coated with a metal layer as described in detail above.

Also shown in FIG. 1C is an alternate configuration of metal electrode 16'. In this configuration, metal electrode 16' comprises a plurality of discrete metal electrodes 16'a, 16'b, and 16'c that may be the same or different metals. Thus, for example, metal electrodes 16'a, 16'b, and 16'c may be the same or different metals and may be respectively paired with semiconductor electrodes 34a, 34b, and 34c to form three electrochemical cells. The electrochemical characteristic of choice for each electrochemical cell thus formed may be individually monitored by separate detectors 24a, 24b, 24c, respectively.

In addition, a separate chamber-encased reference electrode as described above can be incorporated into sensor 10c to provide for the measurement of an additional component of the gas mixture.

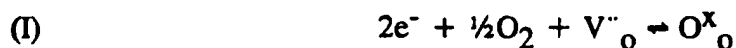
The electrolyte component of the sensor may be fabricated using conventional ceramic processing techniques. Electrode materials may be applied to the surface of the electrolyte using any of a variety of methods well known in the art including sputtering, screen printing, dipping, painting, and the like. Each electrode incorporates an electrical lead by which it can be attached to a monitoring device.

Optionally, a temperature control device capable of heating the sensor to provide temperature regulation thereof is incorporated in the sensor. Preferably the temperature control device comprises a heating element, e.g., a resistance wire, that is incorporated into the electrolyte or on the surface of the electrolyte, to which a power source is connected, or any type of heating element well known in the art.

While not wishing to be bound by theory, the present electrochemical cell is believed to function by the following mechanism. Introduction of oxidizing or reducing gases onto a semiconducting material results in a change in the conductivity or resistivity of the material. For example, Morita et al., *supra*, observed that NO and NO₂ gases cause opposite changes in resistivity of La₂CuO₄, a p-type semiconducting oxide. It is believed that this phenomenon is due to injection of an electronic charge into the semiconducting

material when the gas is adsorbed on the surface. As a result, exposure of a perovskite oxide semiconducting material to NO_x , CO_x or SO_x causes a shift of the equilibrium of the following reaction within the lattice structure of the material:

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10 in which e^- is an electron, $V_{\text{O}}^{\cdot\cdot}$ represents a vacant oxygen site have a valence of +2 and O_{O}^x represents a full oxygen site. When a sensor of the present invention is exposed to a gas mixture such that both the semiconducting electrode and the metal electrode are exposed to the same gas, the metal electrode will not display a change in conductivity or resistance. In fact, the metal electrode will only react to

15 changes in the oxygen partial pressure (" pO_2 ") in the gas mixture, thereby acting as a relative reference, or equilibrium, electrode. By contrast, for example, an electrode comprising La_2CuO_4 is responsive to NO. Upon adsorption of NO, electrons are injected into the La_2CuO_4 resulting in a shift to the right in the equilibrium shown in equation (I), thereby increasing the oxygen activity at the

20 electrode. Because both the semiconducting electrode and the metal electrode are exposed to the same gas stream, and the same fluctuations in pO_2 , and because only the semiconducting electrode is responsive to the oxidizing or reducing gases in the gas mixture, a voltage difference can be measured across the two electrodes that is proportion to the concentration of NO_x , CO_x or SO_x in the gas mixture.

25 Unlike sensors described in the art that depend on the selective catalytic reduction, decomposition or other change in state of the gases to be measured, the present sensor is believed to function without any catalytic alteration of components of the gas mixture.

30

It is to be understood that while the invention has been described in conjunction with the preferred specific embodiments thereof, that the

foregoing description as well as the examples which follow are intended to illustrate and not limit the scope of the invention. Other aspects, advantages and modifications within the scope of the invention will be apparent to those skilled in the art to which the invention pertains.

5

EXPERIMENTAL

The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how to use the invention, and is not intended to limit the scope of what the inventors regard as there invention. Efforts have been made to ensure accuracy with respect to numbers (e.g., amounts, temperature, etc.) but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by volume, temperature is in °C and pressure is at or near atmospheric.

15

Example I

Detection of NO in a Gas Mixture using La_2CuO_4

To evaluate a sensor configured as depicted in FIG. 1A the following studies were conducted. Specifically, such a sensor was fabricated in which the semiconductor electrode was La_2CuO_4 , the metal electrode was platinum, and the electrolyte was yttria-stabilized zirconia. The tests were run at 700°C.

20

FIG. 2 depicts the sensor signal in millivolts in response to various NO concentrations ranging from approximately 100 parts per million ("ppm") to 2500 ppm in 25% O_2 . These data indicate that the sensor is sensitive to parts-per-million amounts of NO even in the presence of high concentrations of O_2 .

25

The ability of the sensor to selectively detect NO is demonstrated in FIG. 3. The data in FIG. 3 shows that the response of the sensor as a function of NO concentration in a gas mixture with 25% O_2 (the slope of line (a)) is more than five hundred-fold greater than that of the response of the sensor

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as a function of O₂ concentration at a fixed NO concentration of 500 ppm (the slope of line (b)).

FIG. 4 depicts the response of the sensor as a function of NO concentration (from 0 to 100 ppm) in the presence of 13% O₂, 15% O₂, or 17% O₂ in a simulated exhaust gas composed of a humidified (2% H₂O) mixture of 10% CO₂, 1000 ppm CO and the balance N₂. These data demonstrate that the sensor can be operated to detect NO with great sensitivity in an exhaust gas mixture with only minimal interference from fluctuations in O₂ concentrations.

FIG. 5 depicts the response of the sensor as a function of NO concentration (from 0 to 100 ppm) in the presence of 1000 ppm CO or 2000 ppm CO in a simulated exhaust gas composed of a humidified (2% H₂O) mixture of 15% O₂, 10% CO₂ and the balance N₂. These data demonstrate that the sensor can be used to detect NO with great sensitivity in an exhaust gas mixture without significant interference from CO concentration fluctuations.

FIG. 6 depicts the response of the sensor to a pulse of NO in a simulated exhaust gas composed of a humidified mixture of 15% O₂, 1000 ppm CO, 10% CO₂ and the balance N₂. After achieving a stable response to the gas mixture containing 0 ppm NO, the exhaust gas was changed to one further containing 50 ppm NO. After the NO response appeared to reach a plateau, the gas mixture was changed back to one without NO. The rapid increase and decrease in sensor signal indicates that the sensor provides a rapid, reversible response to changes in NO concentration.

Example II

Detection of NO in a Gas Mixture

Using (La_{0.8}Sr_{0.2})(Co_{0.9}Ru_{0.1})O₃

To further evaluate a sensor configured as depicted in FIG. 1A the following studies were conducted. Specifically, a sensor was fabricated as described in Example I in which the semiconductor electrode was (La_{0.8}Sr_{0.2})(Co_{0.9}Ru_{0.1})O₃, the metal electrode was platinum, and the electrolyte was yttria-stabilized zirconia. The tests were run at 700°C. Results obtained with this sensor are shown in FIG. 7 and FIG. 8.

FIG. 7 depicts the response of the sensor as a function of NO concentration (from 0 to 100 ppm) in a simulated exhaust gas composed of a humidified (2% H₂O) mixture of 13% O₂, 10% CO₂, 2000 ppm CO and the balance N₂. These data demonstrate that the sensor can be operated to detect NO with great sensitivity in an exhaust gas mixture with only minimal interference from fluctuations in O₂ concentrations. These data indicate that the sensor is sensitive to parts-per-million amounts of NO even in the presence of high concentrations of O₂.

FIG. 8 depicts the response of the sensor to a pulse of NO in a simulated exhaust gas composed of a humidified mixture of 15% O₂, 1000 ppm CO, 10% CO₂ and the balance N₂. After achieving a stable response to the gas mixture containing 0 ppm NO, the exhaust gas was changed to one further containing 50 ppm NO. After the NO response appeared to reach a plateau, the gas mixture was changed back to one without NO. The rapid increase and decrease in sensor signal indicates that the sensor provides a rapid, reversible response to changes in NO concentration.

Example III

Detection of NO in a Gas Mixture

La₂CuO₄ Coated with Platinum

A sensor is prepared as described in Example I in which the exposed surface of the La₂CuO₄ electrode is coated with platinum using a platinum-containing ink.

It is expected that the addition of the platinum coating will increase the signal-to-noise ratio and the NO selectivity.

WE CLAIM:

1. A electrochemical cell for measuring the concentration of a component of a gas mixture comprising:
 - 5 a semiconductor electrode having first and second opposing surfaces, comprising a semiconducting material selected so as to undergo a change in resistivity upon contacting the component;
 - a metal electrode having first and second opposing surfaces; and
 - an electrolyte in contact with the second surface of the
 - 10 semiconductor electrode and the second surface of the metal electrode,
 - wherein when the first surface of one of the electrodes contacts the gas mixture, the first surface of the other electrode necessarily contacts the gas mixture as well.
- 15 2. The electrochemical cell of claim 1, further comprising a reference electrode in contact with the electrolyte.
3. The electrochemical cell of claims 1 or 2, further comprising a metal layer on the first surface of the semiconductor electrode.
- 20 4. A electrochemical cell for measuring the concentration of two or more components of a gas mixture comprising:
 - a set of semiconductor electrodes each of which has first and
 - second opposing surfaces and each of which comprises a semiconducting material
 - 25 selected so as to undergo a change in resistivity upon contacting the components of the mixture, wherein each electrode is selectively responsive to a different component in the mixture;
 - a metal electrode having first and second opposing surfaces; and
 - an electrolyte in contact with the second surface of (a) each
 - 30 electrode of the set of semiconductor electrodes and (b) the first metal electrode.

5. The electrochemical cell of claims 1 or 4, wherein the semiconducting material comprises a metal oxide.

5 6. The electrochemical cell of claim 5, wherein the metal oxide is a perovskite.

7. The electrochemical cell of claim 6, wherein the perovskite is La_2CuO_4 or $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Co}_{0.9}\text{Ru}_{0.1})\text{O}_3$.

10 8. The electrochemical cell of claims 1 or 4, wherein the metal electrode comprises a noble metal.

9. The electrochemical cell of claim 4, further comprising a reference electrode in contact with the electrolyte.

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10. The electrochemical cell of claims 4 or 9, further comprising a metal layer on the first surface of one or more electrode in the set of semiconducting electrodes.

20 11. The electrochemical cell of claims 1, 2, 4 or 9, wherein the electrolyte is an oxygen ion-conducting electrolyte.

12. A method for measuring a concentration of a component of a gas mixture comprising,

25 (a) exposing the gas mixture to an electrochemical cell comprising:

a semiconductor electrode having first and second opposing surfaces, comprising a semiconducting material selected so as to undergo a change in resistivity upon contacting the component;

30 a metal electrode having first and second opposing surfaces; and an electrolyte in contact with the second surface of the semiconductor electrode and the second surface of the metal electrode,

wherein when the first surface of one of the electrodes contacts the gas mixture, the first surface of the other electrode necessarily contacts the gas mixture as well, and

5 (b) measuring an electrical characteristic associated with the semiconductor electrode and the metal electrode to determine the concentration of the component of the gas mixture.

10 13. The method of claim 12, wherein the first surface of the semiconductor electrode is coated with a metal layer.

14. A method for measuring a concentration of two or more components of a gas mixture comprising,

(a) exposing the gas mixture to an electrochemical cell comprising:

15 a set of semiconductor electrodes each of which has first and second opposing surfaces and each of which comprises a semiconducting material selected so as to undergo a change in resistivity upon contacting the components of the mixture, wherein each electrode is selectively responsive to a different component in the mixture;

20 a metal electrode having first and second opposing surfaces; and an electrolyte in contact with the second surface of (i) each electrode of the set of semiconductor electrodes and (ii) the first metal electrode, and

25 (b) measuring an electrical characteristic associated with one or more electrode in the set of semiconducting electrodes and the metal electrode to determine the concentration of the components of the gas mixture.

30 15. The method of claim 14, wherein the first surface of one or more electrode in the set of semiconducting electrodes is coated with a metal layer.

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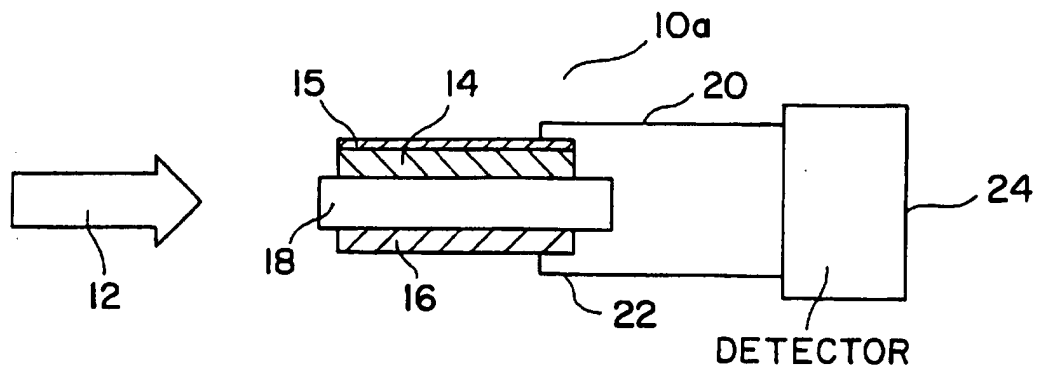


FIG. 1A

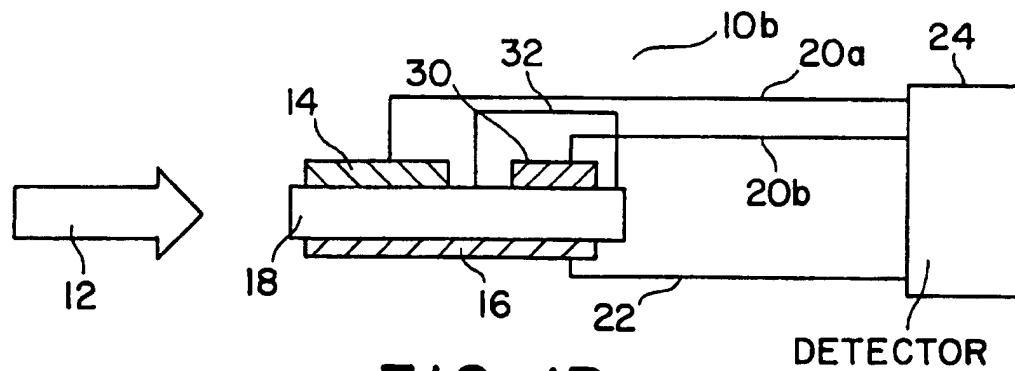


FIG. 1B

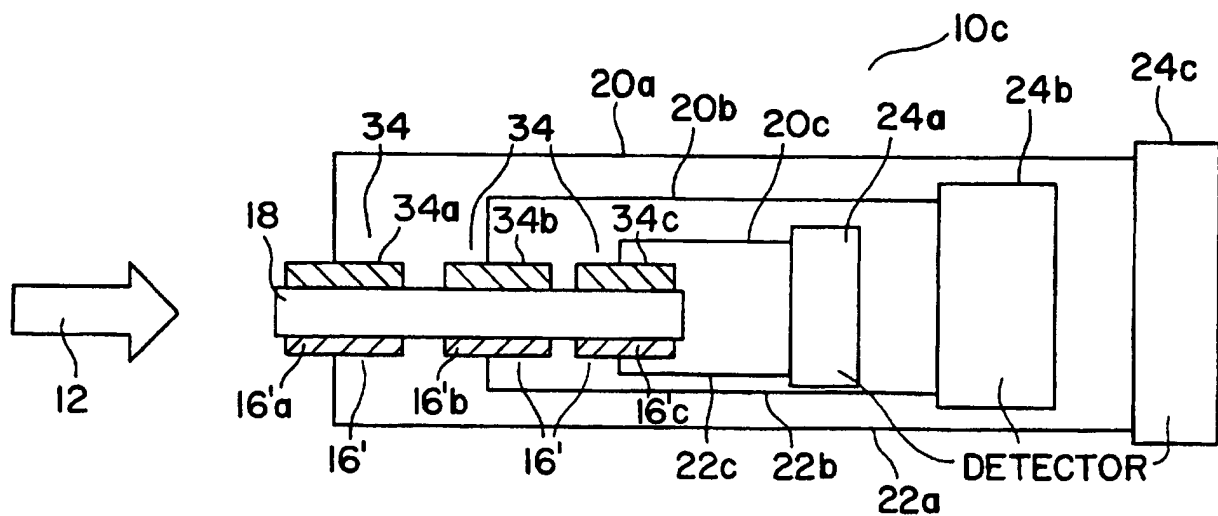


FIG. 1C

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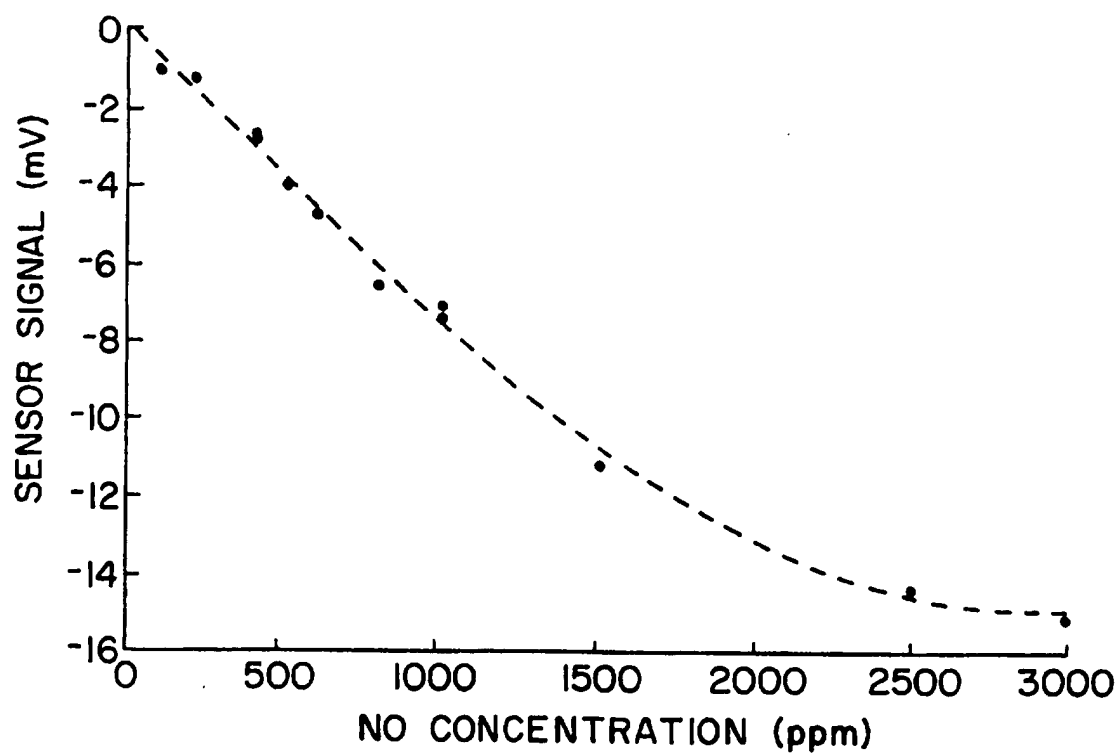


FIG. 2

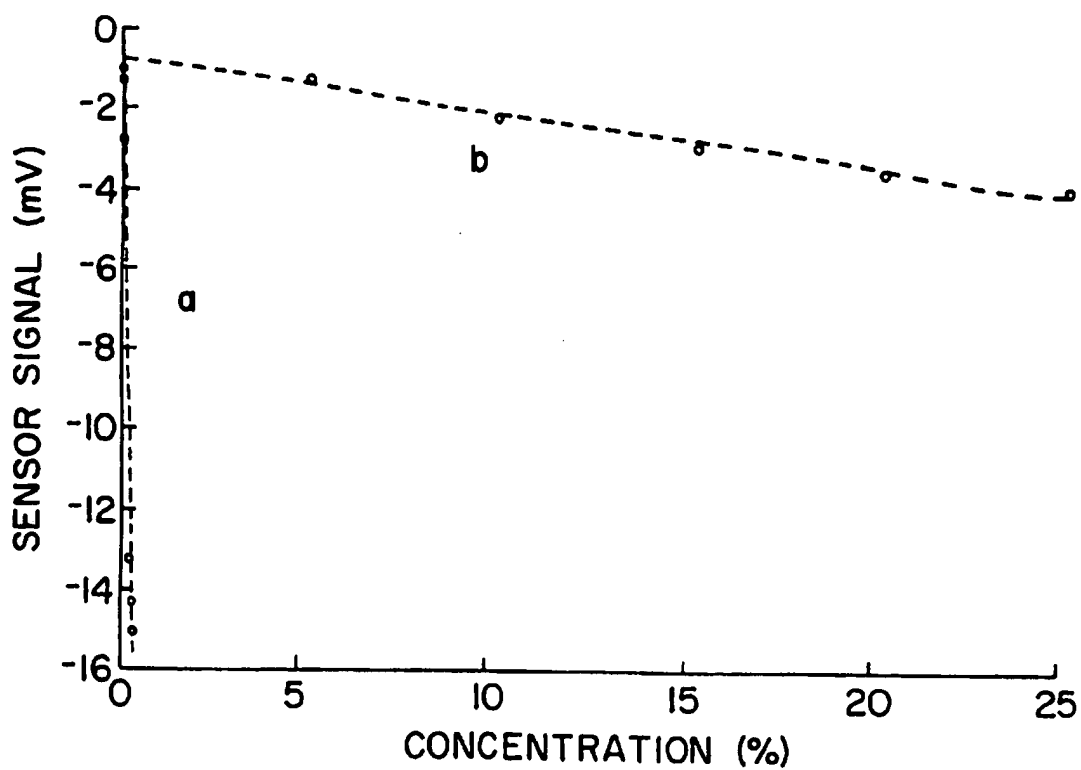


FIG. 3

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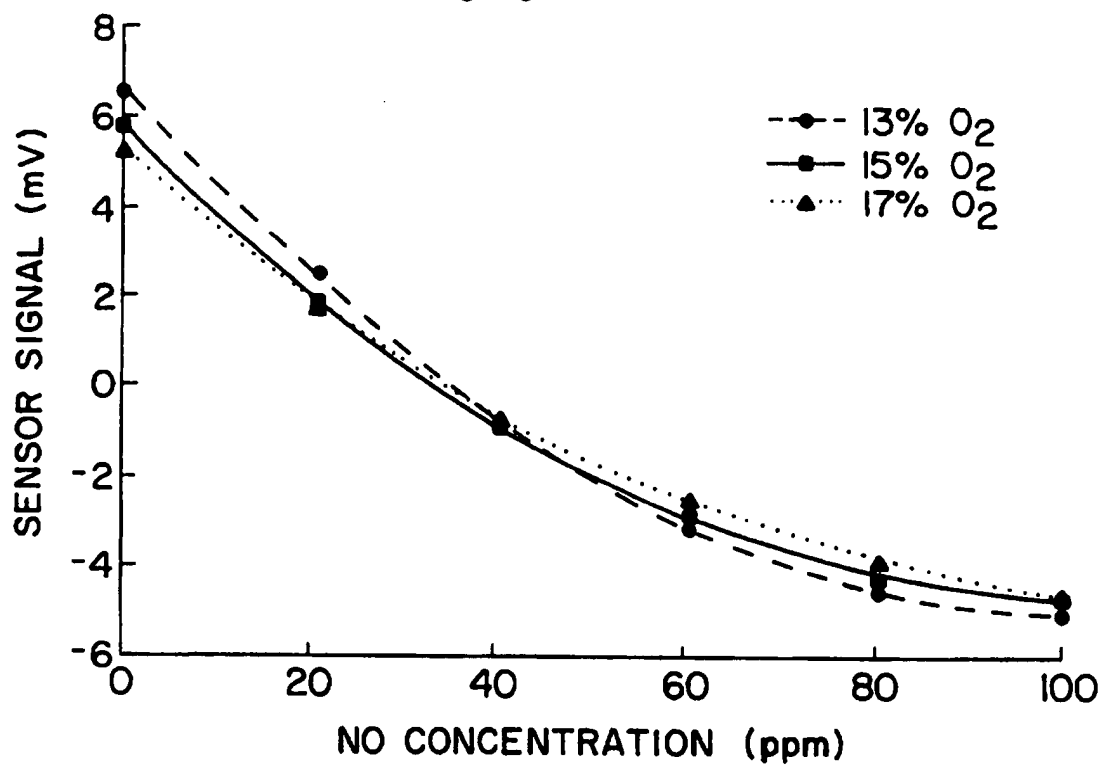


FIG. 4

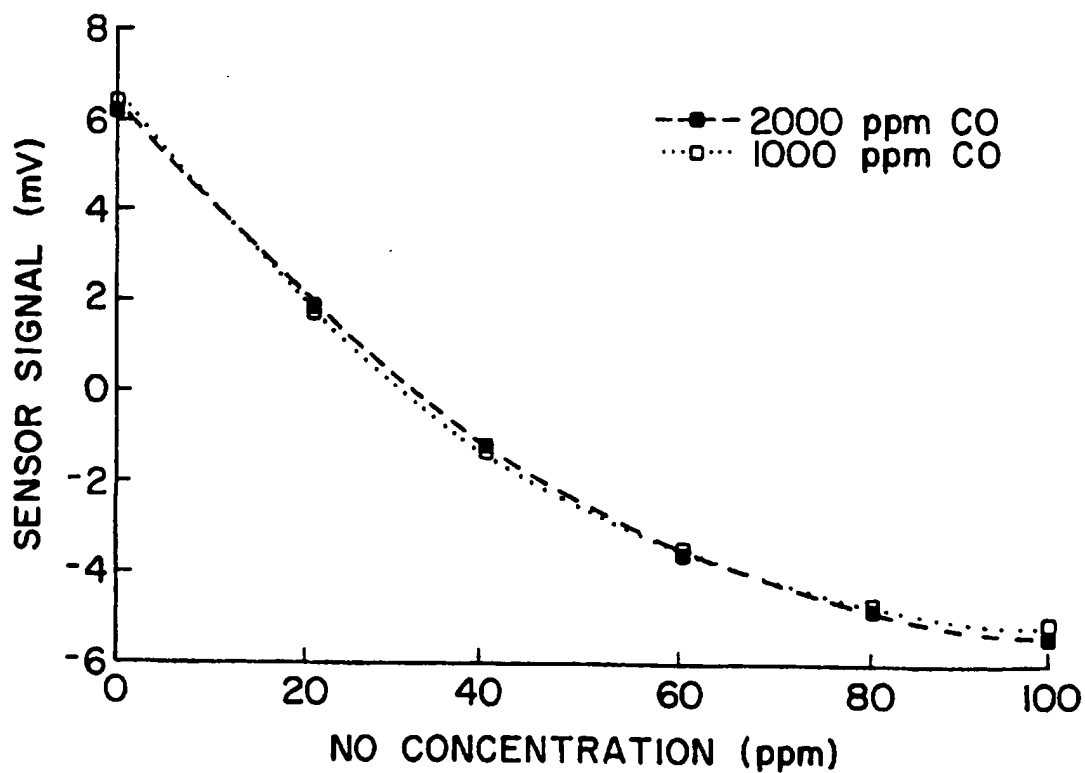


FIG. 5

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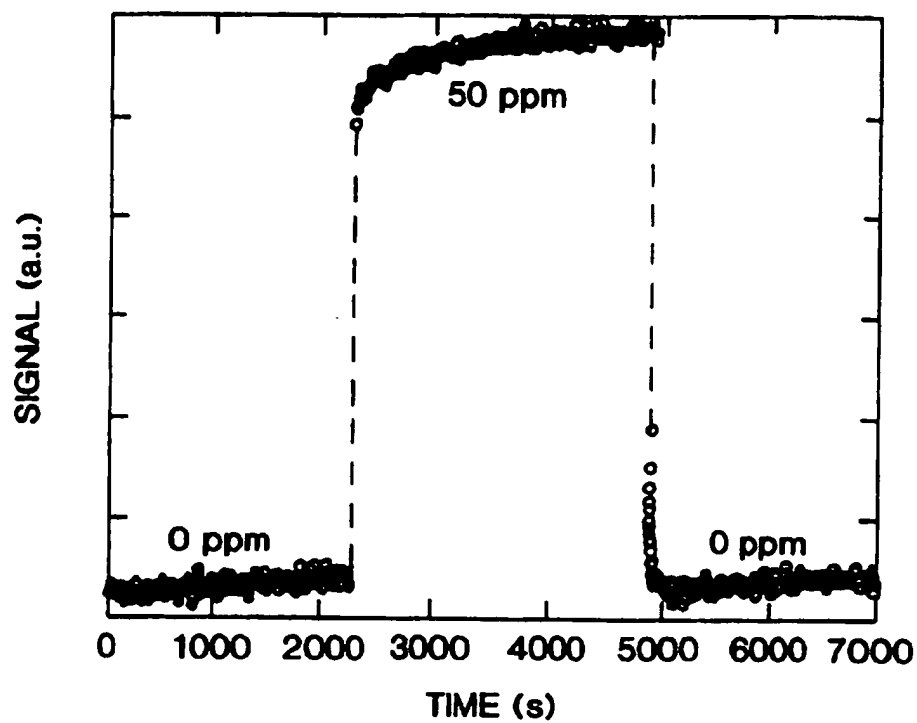


FIG. 6

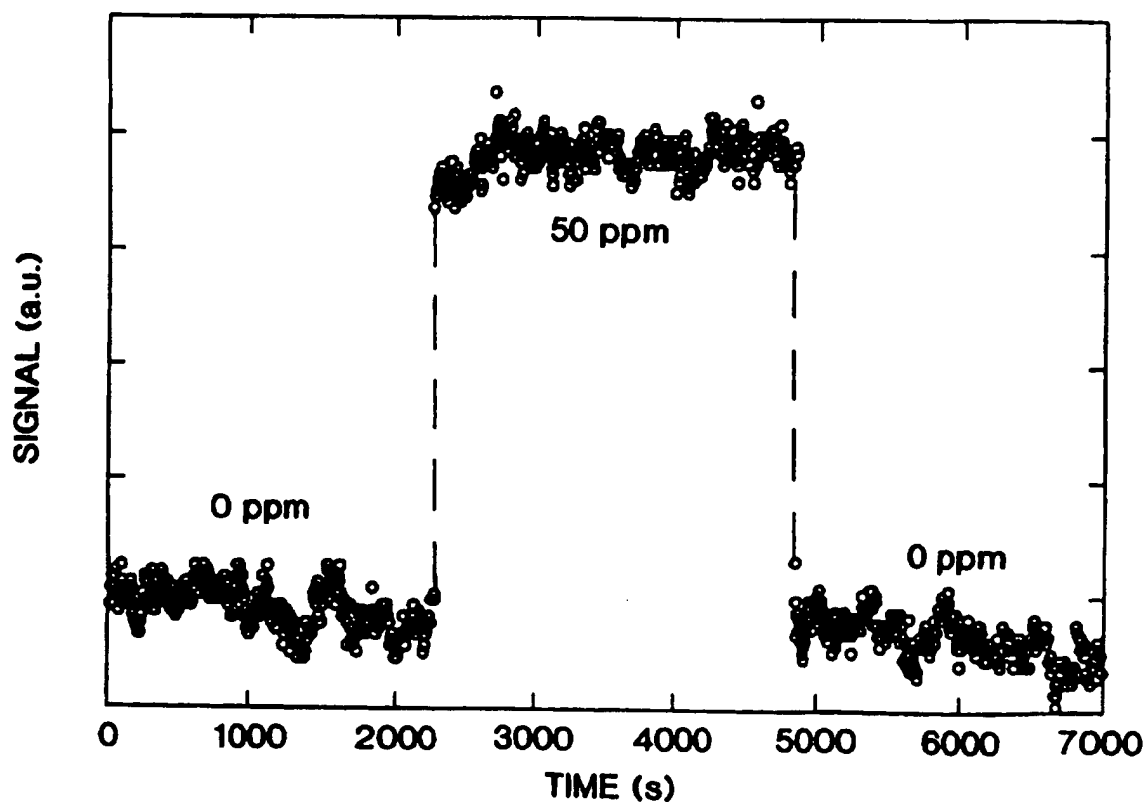


FIG. 8

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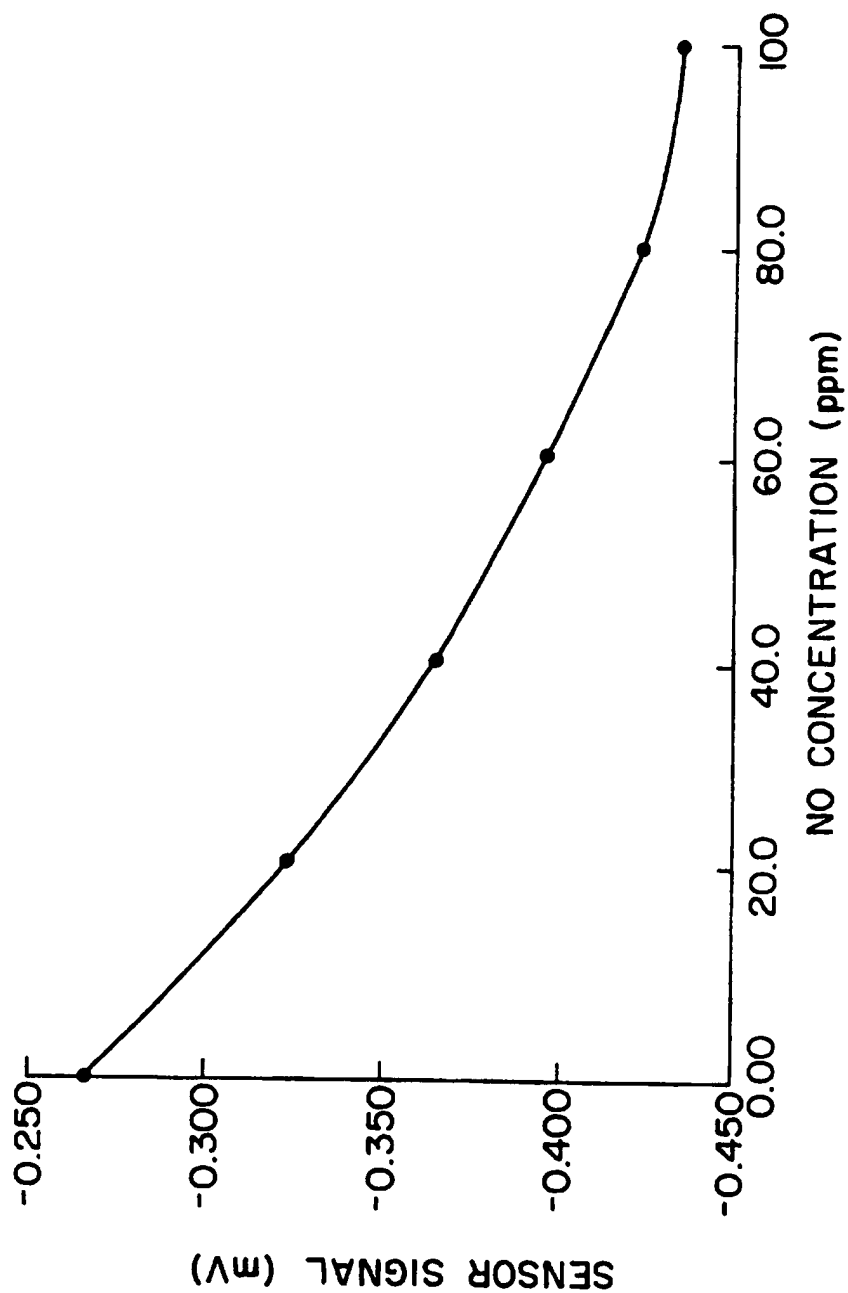


FIG. 7

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/07622

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G01N27/407

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G01N H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 186 090 A (ATOMIC ENERGY AUTHORITY UK) 5 August 1987 see abstract; claims ---	1,3,5,6, 8,11-13
P,X	DE 44 42 272 A (ROTH TECHNIK GMBH) 30 May 1996 see abstract ---	1,4-6, 11,12,14
X	DE 42 25 775 A (HAEFELE UMWELTVERFAHRENSTECHNI) 10 February 1994 see claims ---	1,6,11
A	WO 95 14226 A (CERAMATEC INC) 26 May 1995 see page 11, line 26 - page 12, line 15 ---	1,4
A	US 4 702 971 A (ISENBERG ARNOLD O) 27 October 1987 see column 3, line 20 - column 4 ---	1
	-/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

25 August 1997

Date of mailing of the international search report

01/09/1997

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

CALLEWAERT, H

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/07622

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FR 2 511 154 A (EURATOM) 11 February 1983 see page 2, line 1 - line 13 ----	1
A	US 5 397 442 A (WACHSMAN ERIC D) 14 March 1995 cited in the application ----	
A	NORIO MIURA ET AL: "USE OF OXIDE ELECTRODES FOR PROTON-CONDUCTOR GAS SENSOR" SOLID STATE IONICS, vol. 40 / 41, 1 August 1990, pages 452-455, XP000166173 ----	
A	ALCOCK C B ET AL: "PEROVSKITE ELECTRODES FOR SENSORS" SOLID STATE IONICS, vol. 51, no. 3 / 04, 1 April 1992, pages 281-289, XP000359473 ----	
A	R.H. WILSON ET AL: "Characterized Semiconductor Electrodes" J. ELECTROCHEM. SOC.: SOLID-STATE SCIENCE AND TECHNOLOGY, May 1979, pages 844-850, XP000674338 -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/07622

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2186090 A	05-08-87	NONE	
DE 4442272 A	30-05-96	CZ 9603518 A WO 9617242 A	12-03-97 06-06-96
DE 4225775 A	10-02-94	DE 59304540 D WO 9403795 A WO 9403796 A EP 0606456 A ES 2098050 T JP 6511560 T	02-01-97 17-02-94 17-02-94 20-07-94 16-04-97 22-12-94
WO 9514226 A	26-05-95	NONE	
US 4702971 A	27-10-87	CA 1291788 A DE 3785794 A EP 0253459 A JP 62281271 A US 4812329 A	05-11-91 17-06-93 20-01-88 07-12-87 14-03-89
FR 2511154 A	11-02-83	BE 894044 A DE 3229931 A GB 2104666 A LU 84328 A	01-12-82 17-02-83 09-03-83 28-02-83
US 5397442 A	14-03-95	US 5643429 A	01-07-97